# PHOSPHATES AND POLYPHOSPHATES OF THE RARE EARTHS

BY

ARCHIE GIRARD BUYERS

B.S., Haverford College, 1943
M.S., University of Illinois, 1947

## AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

URBANA, ILLINOIS

1950

# PHOSPHATES AND POLYPHOSPHATES OF THE RARE EARTHS

BY

ARCHIE GIRARD BUYERS

B.S., Haverford College, 1943
M.S., University of Illinois, 1947

## AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

URBANA, ILLINOIS

1950

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor L. F. Audrieth for his advice and help in directing the course and progress of this investigation.

He would also like to thank Dr. R. Johnson for his aid in the application of statistical methods to the rare earth average atomic weight determinations.

It is desired to express appreciation to Mrs. E. B. Mohr for her analytical work and contributions to the investigation of the average atomic weights of rare earth mixtures.

The author is grateful to the Office of Naval Research whose grant of funds to the University of Illinois made this investigation possible.

R. UNIV.
BIBLIOTHEEK
LEIDEN

# I. DETERMINATION OF THE AVERAGE ATOMIC WEIGHT OF RARE EARTH MIXTURES

## Introduction

The rare earth series is composed of fifteen chemically similar elements whose atomic weights vary in small increments from 139 to 175 atomic weight units. The homologous chemical nature and the closely related values of atomic weight make difficult rare earth analyses for the purpose of following any fractional separation procedure. Three methods have found application:

1.) Spectrophotometric analysis is used for those rare earths which have suitable absorption spectra.

2.) Radioactive tracer techniques are used to follow rare earth separation by ion exchange.

3.) Average atomic weight determinations of rare earth mixtures is applicable to most rare earths.

In the present investigation the accepted standard permanganate procedure (1) was compared with data obtained by use of two new methods i.e., a cerate procedure and a phosphate method. The cerate procedure is similar to the standard permanganate, except that the oxalate ion is titrated with standard cerate solution in perchloric acid medium using nitro ferroin as indicator. (2) The phosphate method is based on measurement of released hydrogen ion from a mixture of rare earth and sodium dihydrogen phosphate solutions each adjusted to pH 4.5 prior to mixing. Results obtained by applying these three methods were subjected to a statistical comparison.

## Experimental and Results

### A. Determination of the average atomic weight of rare earth mixtures by the permanganate method

Experimental application of the standard permanganate

procedure for the determination of average atomic weights of rare earth mixtures was made upon a series of rare earth oxalates intended to represent the entire rare earth group.

This method was found to be well adapted for such determinations provided the following conditions are met:

1.) The permanganate method is employed as outlined in reference (1) ; better reproducibility is achieved if the modification recommended by Fowler and Bright (3) is used. This modification consists of adding to the cold solution approximately 95% of the total permanganate needed for a titration, heating this mixture to 55-60° C and completing the titration.

2.) The rare earth oxalate should be reprecipitated and ground in an agate mortar followed by thorough mixing. (4)

3.) Care is taken in the precipitation of the yttrium earth oxalates to prevent formation of the double rare earth-ammonium oxalates.

## B. CERIOMETRIC DETERMINATION OF THE OXALATE CONTENT OF RARE EARTHS FOR DETERMINATION OF AVERAGE ATOMIC WEIGHTS

Average atomic weight determinations employing a cerate titration of oxalate ion in perchloric acid medium using nitroferroin as indicator were carried out upon the same rare earths which had been subjected to the standard permanganate determination. Here it is again necessary to observe the precautions 2.) and 3.) for the standard permanganate method.

Since the cerate titration may be carried out at room temperature it is easier to execute experimentally than the permanganate.

### C. STATISTICAL ANALYSIS OF CERATE AND PERMANGANATE AVERAGE ATOMIC WEIGHT DATA

Four statistical techniques were used for comparison of the average atomic weight results obtained from determinations by the permanganate and cerate methods. These were:

1.) analysis of variance, (5)

2.) the "F" test for homogeneity of variances, (6)

3.) the "t" test for comparison of mean results, (7)

4.) the setting of fiducial limits for evaluation of precision within which each method and each individual operation can be employed. (8)

This statistical treatment led to the following conclusions:

1.) The operation primarily responsible for variations in atomic weights within a given series is ignition of the oxalate to the oxide.

2.) There is no significant difference between the means obtained by permanganate and cerate titrations of oxalate ion.

3.) The permanganate method is more precise than the cerate method.

4.) If three determinations of average atomic weight are performed by the standard permanganate procedure, the mean of three atomic weight values will not deviate from the true mean by more than $\pm$ 1.28 atomic weight units in ninety five percent of cases.

5.) If three determinations are performed by the cerate method, the mean of three atomic weight values will not deviate from the true mean by more than $\pm$ 2.28 atomic weight units.

### D. DETERMINATION OF THE AVERAGE ATOMIC WEIGHT OF RARE EARTH MIXTURES BY THE PHOSPHATE METHOD

A series of average atomic weight determinations were carried out upon a group of rare earths similar to those

employed for the cerate and permanganate determinations. This method is based upon the measurement of released acidity at pH 4.5 represented by the equation:

$$1.)\ R^{+3} + H_2PO_4^{-1} \longrightarrow \underline{RPO_4} \downarrow + 2H^{+1}$$

In the majority of cases average atomic weights determined by this method were higher than those obtained from parallel determinations by the permanganate method. This observation indicated incomplete liberation of hydrogen ion. Attempts were made to achieve quantitative release of acidity as represented by equation 1.) by a) variations in rare earth concentration, b) conditions of precipitation, c) addition of competitive adsorption agents, and d) titration to an indicator endpoint. These efforts were unsuccessful.

The buffering effect of varying excesses of phosphate reagent upon the back-titration end-point was evaluated. This investigation disclosed that the selection of a pH 4.5 for adjustment and titration purposes was thoroughly justified and preclude the use of any other pH.

Variations in atomic weight values and statistical treatment of the data obtained cause rejection of this method as an average atomic weight procedure.

## BIBLIOGRAPHY

1. Fernelius, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., 1946, Vol. 2, p. 58-61.

2. Smith, "Cerate Oxidimetry," G. Frederick Smith Chemical Co., Columbus, Ohio, 1942, p. 37-39, 79-82.

3. Fowler, and Bright, J. Research Nat. Bur. Standards, 15, 493 (1935).

4. Gibbs, Am. Chem. J., 15, 546 (1893).

5. Snedecor, "Statistical Methods," Iowa State College Press, Ames, Iowa, 1946, Ed. 4, p. 215.

6. Snedecor, ibid., 219-226.

7. Snedecor, ibid., 43-46.

8. Snedecor, ibid., 41-42.

## II. THE PHOSPHATES AND POLYPHOSPHATES OF THE RARE EARTHS AND THORIUM

### Introduction

The investigation of the phosphates and polyphosphates of the rare earths and thorium was undertaken in order to:

1.) Characterize the phosphates and polyphosphates of the rare earths and thorium.

2.) Develop a method for the separation of thorium from the rare earths by application of differences in the properties of the respective phosphates and polyphosphates.

3.) Identify the phosphate species formed during the treatment of an ore such as monazite.

Recorded information concerning the phosphates and polyphosphates of the rare earths has been examined critically and found to reveal many discrepancies. Since rare earth and phosphate analyses of such products are difficult, more direct procedures were desired. One such method involved the hydrogen ion displacement technique developed in PART I of this thesis. Gravimetric determinations of the precipitated reaction products were also carried out. pH and conductometric titration measurements indicated two additional approaches, based on results achieved in the following investigations:

1.) the mechanism of silver phosphate precipitation, (1)

2.) the formation of basic phosphates in the precipitation of lanthanum phosphate with various orthophosphate reagents, (2)

3.) the nature of products formed when solutions of ferric and orthophosphate ions were allowed to react, (3)

4.) complex formation between cupric and pyrophosphate ions in solution, (4)

5.) complex formation between various multivalent cations and pyrophosphate ion, (5)

The information concerning the phosphates and polyphosphates of thorium which is found in the literature is likewise fragmentary. Since thorium will precipitate as a hydrous oxide from aqueous solution at a pH slightly above 3.0, the hydrogen ion displacement technique cannot be employed. However, pH and conductometric titration measurements offered a direct method for characterizing the precipitation products of reactions between thorium and various phosphate reagents. Frankenthal, and co-workers (6) have indicated the existence of thorium-triphosphate soluble complexes and it was thought that pH and conductometric titrations might reveal the nature of these ions.

## Experimental and Results

### A. The Phosphates and Polyphosphates of the Rare Earths

#### *1. Orthophosphates of The Rare Earths*

Application of the technique of measuring released hydrogen ion at a pH of 4.5 disclosed that the following equation represents essentially the reaction which occurs upon mixing rare earth and sodium dihydrogen phosphate solutions adjusted to this pH:

$$1.)\quad R^{+3} + H_2PO_4^{-1} \longrightarrow \underline{RPO_4\downarrow} + 2H^{+1}$$

Slightly low measured values of released acidity and gravimetric determination by ignition of products at 900° C suggest initial contamination of precipitates with a small amount of a rare earth hydrogen phosphate which is converted to rare earth pyrophosphate upon ignition.

$$2.)\ 2R^{+3} + 3H_2PO_4^{-1} \longrightarrow \underline{R_2(HPO_4)_3}\downarrow + 3H^{+1}$$

$$3.)\ \underline{2R_2(HPO_4)_3} \xrightarrow{\Delta} \underline{R_4(P_2O_7)_3}\downarrow + 3H_2O$$

Formation of the small amount of a rare earth hydrogen phosphate would explain low values of released hydrogen ion and would account for the fact that experimental weights of ignited precipitates were slightly larger than demanded by theory.

X-ray powder patterns of ignited precipitates were identical with those obtained from finely ground monazite sand in which the rare earth is known to exist as an orthophosphate.

Simultaneous pH and conductometric titration of rare earth with di- and trisodium phosphate reveal that orthophosphates were precipitated in each case.

*2. Pyrophosphates of The Rare Earths*

The technique of back titration of released acidity to a given pH, i. e., 4.5 was also applied to an investigation of rare earth pyrophosphates. The reaction can be represented by the equation:

$$4.)\ 4R^{+3} + 3H_2P_2O_7^{-2} \longrightarrow \underline{R_4(P_2O_7)_3}\downarrow + 6H^{+1}$$

Measurement of released hydrogen ion yielded values approximating that demanded by the above equation.

Heating the suspension of the rare earth pyrophosphate in its mother liquor results in conversion of the precipitate to the orthophosphate. The overall reaction for hydrolysis of the precipitate suspended in its mother liquor may be represented at pH 4.5 by the following equation:

$$5.)\ 4R^{+3} + 3H_2P_2O_7^{-2} + 3H_2O \rightleftarrows \underline{4RPO_4}\downarrow + 2H_2PO_4^{-1} + 8H^{+1}$$

Conversion to an orthophosphate is also caused by hydrolysis of the precipitate as indicated by the fact that a suspension

of the precipitated pyrophosphate in water at a pH 4.5 and subsequent heating results in liberation of titratable acidity.

$$6.)\ \underline{R_4(P_2O_7)_3}\downarrow + 3H_2O \rightleftharpoons \underline{4RPO_4}\downarrow + 2H_2PO_4^{-1} + 2H^{+1}$$

In both instances the hydrogen ion/rare earth ratio approached that required for quantative conversion to the orthophosphate.

Initial weights of rare earth pyrophosphates, ignited at 900° C, agreed closely with theory, but long extended heating of these materials disclosed small losses in weight. X-ray powder patterns of precipitation products of ignited ortho- and pyrophosphates were identical indicating that both materials were primarily orthophosphates. It was possible that the hydrated rare earth pyrophosphate released phosphoric acid or phosphorous (V) oxide upon ignition to yield an orthophosphate.

Simultaneous pH and conductometric titrations, involving titration of the rare earth solution with the pyrophosphate demonstrated that the normal rare earth pyrophosphate was formed. However, in the pH range 8.0-10.0, in the presence of a large excess pyrophosphate reagent, a soluble rare earth-pyrophosphate complex was formed. Reversal of the titration procedure indicated that the complex ion corresponds to the composition $(RP_2O_7)^-$.

*3. Triphosphates of The Rare Earths.*

The nature of the reaction between solutions of the sodium triphosphate and solutions of rare earth salts using the hydrogen ion displacement procedure disclosed that the reaction may be represented by the equation:

$$7.)\ 5R^{+3} + 3H_2P_3O_{10}^{-3} \longrightarrow \underline{R_5(P_3O_{10})_3}\downarrow + 6H^{+1}$$

Simultaneous pH and conductometric titrations, titrating rare earth solution with triphosphate, and employing the reverse procedure demonstrated:

1.) A normal rare earth triphosphate was formed at a pH of 4.5.

2.) No precipitate was formed in a rare earth-triphosphate mixture at pH 1.0 on standing for one month unless heated.

3.) In the presence of a large excess of triphosphate reagent and over the pH range 7.0-8.5 a soluble rare earth-triphosphate complex was formed.

Rare earth hydroxides are sequestered by excess triphosphate only over a limited pH range. Suspensions of $Nd(OH)_3$ in triphosphate (pH 9.5-10.0) can be brought into solution by lowering the pH to approximately 8.0. This suggested competitive equilibria which may be represented as follows:

$$8.)\quad P_3O_{10}^{-5} + H_2O \leftrightharpoons HP_3O_{10}^{-4} + OH^{-1}$$

$$9.)\quad \underline{R(OH)_3\downarrow} \leftrightharpoons R^{+3} + 3OH^{-1}$$

$$10.)\quad xR^{+3} + yHP_3O_{10}^{-4} \leftrightharpoons [\text{Complex}]$$

*4. Trimetaphosphates of The Rare Earths*

The information concerning the trimetaphosphates of the rare earths is limited. At a pH of 1.0 the reaction between trimetaphosphate and rare earth ions in aqueous solution yielded no insoluble product. At higher pH values, a precipitate did form gradually, but the precipitation was not immediate and was not complete even after one week.

B. THE PHOSPHATES AND POLYPHOSPHATES OF THORIUM

*1. Ortho-, Pyro-, and Triphosphates of Thorium*

A study of simultaneous pH and conductometric curves, obtained by titration of thorium nitrate solutions with various phosphate reagents (disodium hydrogen phosphate, trisodium phosphate, tetrasodium pyrophosphate, and pentasodium triphosphate) disclosed that thorium will form a normal salt in each case. Reverse titration of tetrasodium pyrophosphate

and pentasodium triphosphate solutions with thorium nitrate revealed that soluble complexes were formed. These complexes were formed at pH above 7.0 for thorium-pyrophosphate mixtures and at a pH above 5.0 for thorium-triphosphate mixtures.

Thorium ion and triphosphate, both at a pH of 1.0 did react to give a gelatinous precipitate of the hydrated triphosphate.

*2. Trimetaphosphates of Thorium*

Thorium nitrate solutions at pH values of 1.0-3.0 yielded gelatinous precipitates with aqueous trimetaphosphate at the same pH. The precipitation of thorium was nearly quantative after 72 hours. Due to the fact that the hydrolysis of trimetaphosphate takes place rapidly in acid solution and the fact that the reaction was not immediate, attempts to determine the composition of the precipitated material were unsuccessful.

## Summary

1.) The rare earths from normal ortho-, pyro-, and triphosphates under suitable conditions in aqueous solution.

2.) The rare earths will form soluble complexes with pyrophosphate in the pH range 8.0-10.0, with triphosphate in the pH range 7.0-8.5.

3.) The rare earths are not precipitated by either triphosphate or trimetaphosphate at a pH of 1.0.

4.) Thorium will form normal salts with ortho-, pyro-, and triphosphate under suitable conditions in aqueous solution.

5.) Thorium is precipitated in the form of an insoluble normal triphosphate at a pH of 1.0, also quantitatively by trimetaphosphate after 72 hours.

7.) Separation of thorium from the rare earths is theoretically possible by:

a.) Precipitation of thorium at a pH of 1.0 using either

sodium triphosphate or sodium trimetaphosphate.

b.) Formation of a soluble complex of thorium at a pH above 5.0, under which conditions the rare earths form insoluble triphosphates.

8.) Further work is necessary to determine the nature of the soluble complexes of thorium and the rare earths and of the precipitation products of both thorium and the rare earths with trimetaphosphate.

## BIBLIOGRAPHY

1. Hubicki, Ann. Univ. Mariae Curie Sklodowska Lublin, Polonia, Sect. AA, 2 No. 9 153 (1947).

2. Hubicki, ibid., Sect. AA, 2, No. 11, 186 (1947).

3. Hubicki, ibid., Sect. AA, 2, No. 10, 167 (1947).

4. Haldar, Science and Culture, 14, (8), 340 (1949).

5. Rogers and Reynolds, J. Am. Chem. Soc., 71, 2081 (1949).

6. Frankenthal, Neuberg, and Roberts, Exp Med. and Sur. I, 386 (1943).

# VITA

The author was born on February 24, 1923 at Fort Munroe, Virginia. The early part of his life was spent at army posts and as a result he did not enter public schools until the sixth grade. His schooling prior to this grade was conducted by his mother using the course offered by the Calvert School of Baltimore, Maryland. After attending the Payson Park Grade School, Belmont, Massachusetts and Belmont Junior High School, he entered Alice Deal Junior High School, Washington, D. C. from which he was graduated. He then attended The Woodrow Wilson High School, Washington, D. C. After one year in attendance at Dover High School, Dover, New Jersey, he enrolled for his last year of high school at The Hill School, Pottstown, Pennsylvania. While attending The Hill School, he had been awarded a half-tuition scholarship. His high school diploma was awarded by The Hill School in June of 1940. He was awarded the prize for excellence in chemistry upon graduation.

In September, 1940, he entered Haverford College as a freshman. In August of 1943, he received a Bachelor of Science in Chemistry from Haverford College which was awarded with Final Honors. Upon graduation he was appointed co-winner of The Pierce Memorial Prize for senior chemical research.

He spent a period of about seven months working in the research and development department of The Shell Oil Company, Martinez, California. He then spent two months in the process department of The Union Oil Company, Oleum, California.

In May 1944 he was drafted into the United States Naval Reserve. After taking his boot training in San Diego, California, he was sent to the United States Naval Hospital Corps School in San Diego, California.

Upon graduation he was sent to the United States Naval Reserve Midshipmen's School at Columbia University, New York. He was graduated an Ensign of the line in April 1945. The Navy then sent him to United States Navy Submarine Chaser School in Miami, Florida. After graduation, he was sent to the Motor Torpedo Boat Squadrons Training Center, Mellville, Rhode Island. While in attendance there, this school was closed and the author was ordered to Okinawa, to duty aboard the USS YMS 470. He served as deck officer aboard this vessel from early October 1945 until August 1946. After first being assigned duties as engineering, medical and supply officers, he subsequently held the positions of first lieutenant, navigation, gunnery, executive and commanding officer of this ship. He was executive officer during the Pacific crossing from Kobe, Japan, to San Francisco. He served as commanding officer during the attachment of his ship to the nineteenth reserve fleet based at San Diego, California. He was released to inactive duty with an Honorable Discharge on August 20, 1946. He was awarded the World War II Victory Medal, Pacific Theater medal with one star, and the American Theater ribbon.

In September 1946 he entered the graduate school of chemistry at the University of Illinois. In February 1947 he was appointed to a half time research assistantship to work on Navy ONR Chem. Task VII. This position he held until his graduation in 1950. In October 1947 he was awarded an M.S. degree in chemistry by The University of Illinois.

He was married to Bettie Joy Gariepy of Los Angeles, California, on October 23, 1947.

The author is a member of Alpha Chi Sigma, and The American Chemical Society.